Studies on Degradation of PET in Mechanical Recycling

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SUMMARY: PET Poly(ethylene terephthalate) was processed repeatedly in a twin extruder. Effect of reprocessing on molecular structure of PET was evaluated in terms of reduction in molecular weight and mechanical properties. This study shows that weight-average molecular weight M_W drops more notably compared with mechanical properties. Mechanical blending of virgin polymer with recycled PET was studied. The results of mechanical testings indicate that there is only slight loss in mechanical properties. The results suggest that mechanical recycling is a suitable method for recycling of PET for economic and environmental purposes.

Introduction

In its amorphous form, PET Poly(ethylene terephthalate) is a tough and transparent polymer and has been a great success in the bottling of carbonated drinks. The material is a reasonably good gas barrier with no influence on flavour and has a non-toxic nature. By the early 1990s, approximately 13 million tonnes of PET were being produced annually with 1.5 million tonnes finding applications in packaging as bottles and trays [1]. Due to high amount of resulting garbage, recycling of used PET bottles is a major concern in recent years particularly in developing countries in terms of environmental and economic considerations. A number of methods have been adopted for recycling of PET namely incineration, hydrolysis of PET to constituent monomers and mechanical blending [2]. In this paper we have studied the extent of loss in molecular weight and mechanical properties of PET associated with the degradation of polymer in mechanical recycling. The state of crystallinity in recycled materials have been discussed.

Experimental

PET in the form of white pellets were first dried at 120°C for 24h and then fed to a Collin twin extruder model Zweiwellenkneter Nr 5500 in counter-current mode at screw speed of 62 rpm and temperature profile of 235°C to 260°C in plasticating zone. The extrudate as strand was cooled into a water bath and then pelletized. The above procedure was repeated in order to obtain two and three times processed material. The obtained products were called PET1, PET2 and PET3 indicating the number of processing cycles the polymer was gone through. Notched Izod impact test and Tensile test were carried out on the specimens which injection-moulded from virgin and

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recycled PETs at 265°C and 40 kg/cm^2 into a cold mould (10°C) in a cycle time of 60 secs. Blends of virgin PET0 and recycled PET1 were injection moulded in the same way. A Perkin-Elmer Calorimeter was used to study the crystallisation behaviour of the materials at a heating rate of 20°C/min. Molecular weights were determined by viscosity measurements of solutions of the polymer in phenol/tetrachloroethane (60/40 w/w) solvent in a Ubbelohde viscometer at 25°C.

Results and discussion

The measured intrinsic viscosities and molecular weights of the samples as depicted in Table 1 were decreased with further reprocessing. This indicates that the molecular chains of PET undergo thermal degradation on further processing. As the melt viscosity decreases with decrease in molecular weight, it might be predicted that loss in molecular weight after each process, could affect adversely the stretch-blow molding process. Different degradation mechanisms result in molecules with carboxylic and ethylene end-groups which their number can be measured.

Table 1: Variation of molecular parameters of PET with processing.

	PET0	PET1	PET2	PET3
Intrinsic viscosity [μ], dL/g	0.841	0.689	0.632	0.424
Molecular weight M_W	50400	37100	32460	22230
No. of end-groups, meq/kg	71	90	100	134

The impact and tensile strength of the samples (Table 2) also decreased slightly with further processing which is associated with decrease in molecular chain lengths.

Table 2: Variation of mechanical properties of PET with processing.

	Impact strength (J/m)	Tensile strength (MPa)
PET0	24.27	61.37
PET1	21.97	60.54
PET2	21.81	59.28
PET3	21.11	56.42

The results show that decrease in polymer properties with increase in the number of processing cycles are not severe. However, sharp decrease in mechanical properties with excessive processing may be predicted when the molecular weight is under a critical value. The slight decrease in mechanical properties makes the mechanical recycling a promising method for tackling of the huge PET bottle-scraps. It should be noted that the residence time of PET in twin extruder was kept short by setting the direction of rotation in counter-current mode and also increasing the screw rotation speed up to 62 rpm in order to approximate the less severe situation in stretch-blow moulding process. Virgin PET shows no cold crystallisation temperature T_{cc} in DSC thermograms as it is already a crystallised white colour polymer but it occurs in recycled transparent PETs. T_{cc} of the recycled PET decreases with the number of reprocessing while crystallisation temperature T_c of the samples in the cooling cycle after melting increases. T_C of the virgin PET is broad while those of PETs are quite sharp in DSC curves. The decrease in T_{cc} and increase in T_c indicate that in recycled PET crystallisation occurs more easily as the number of reprocessing cycle increases. This may be the result of reduction in polymer chain length due to reprocessing which facilitates crystallisation process. Crystallinity of the samples were calculated from the DSC thermograms. As depicted in Table 3, crystallinity of the samples increase with reprocessing.

Table 3: Thermal analysis measurements of the samples.

	T_g °C	T_{cc} °C	T_m °C	T_c °C	ΔH_c (cal/ g)	Crystallinity %
PET0	78	-	250.6 6	185.0 2	8.65	24.5
PET1	78	140.3 4	253.0 6	196.6	10.44	30.15
PET2	78.6	138.7 6	253.1 1	199.0 5	11.1	32.05
PET3	78.6	135.3 3	253.2 4	200.2 6	11.16	32.22

It should be noted that heats of melting ΔH_m and cold crystallisation ΔH_{cc} may be measured with newly developed modulated DSC which separates reversible and irreversible heats. While with conventional DSC measuring the area at T_m and T_{cc} on the heating run is misleading as the cold crystalisation exotherm and melting endotherm appear as an superimposed curve and thus could lead to erroneous values of ΔH_m and ΔH_{cc}. However the area at T_c on the cooling run is an accurate measure of crystallisation heat ΔH_c. Blends of recycled PET and virgin PET were studied in order to achieve an optimum composition for the blend without loss of desirable properties of PET. Molecular weights and impact strength of PET and PET1 blends are shown in Figures 1-2. The mechanical properties of the blends are only slightly inferior to virgin PET. This is obviously a promising result that makes mechanical blending a practical procedure for recycling purposes. However reprocessed PET shows slightly light brown colour due to degradation.

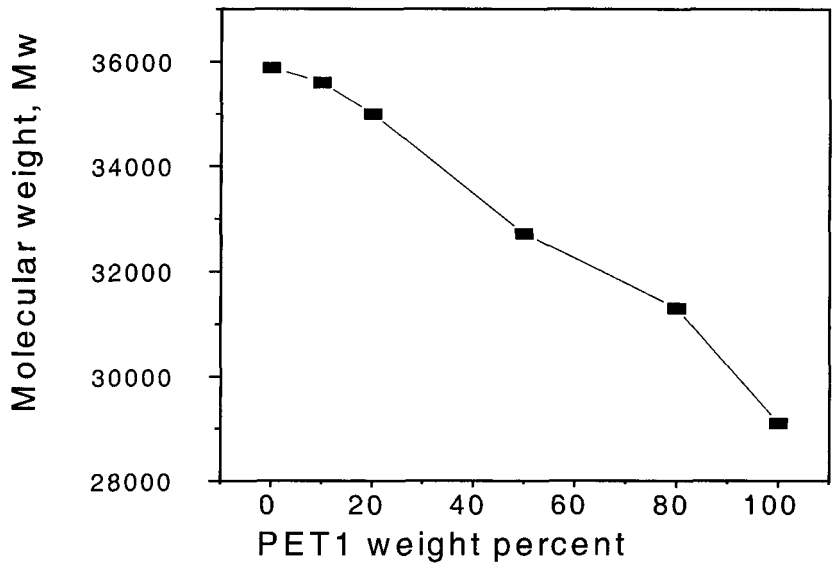

Fig. 1: Weight average molecular weight of blends

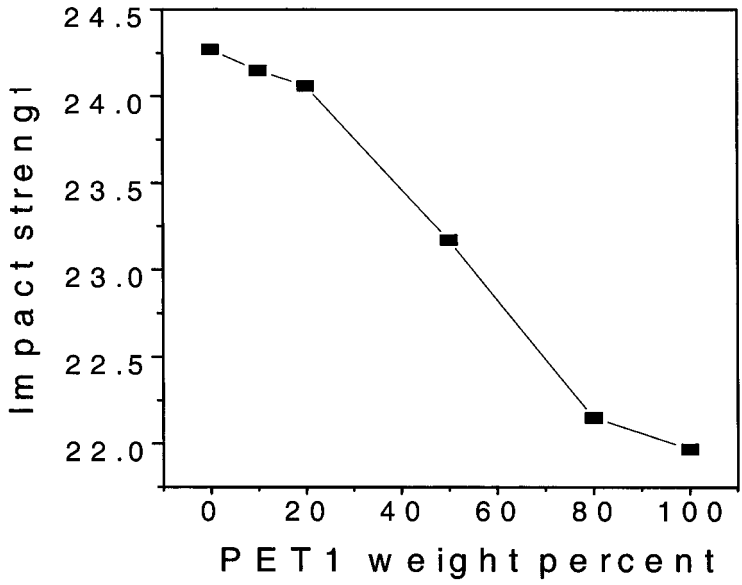

Fig. 2: Mechanical properties of blends

Conclusion

Repeated processing of PET effects slightly the mechanical properties. However decrease in molecular weight is more notable. The decrease in molecular weight can effect negatively the stretch-blow moulding process due to loss in melt viscosity. Addition of recycled PET up to 20 weight percent results in blends which have practically the properties of virgin PET. These results suggest that the mechanical blending is an practical method for recycling of PET in order to reduce the impact of accumlated used-PET bottles in the environment.

References

1)A. Barnetson, *"Plastic Materials for Packaging"*, RAPRA Technology, June 1996.
2)J. Murphy, *"Reinforced Plastics Handbook"*, Elsevier Sciience Publishers, 1994, p 329